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(54) Method of manufacturing organic EL element, organic EL element

Organisches elektrolumineszentes Element und Verfahren zur Herstellung desselben

Elément électroluminescent organique et procédé de fabrication

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- **PATENT ABSTRACTS OF JAPAN** vol. 1997, no. 12, 25 December 1997 (1997-12-25) -& JP 09 203803 A (ASAHI GLASS CO LTD), 5 August 1997 (1997-08-05)
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Description

[0001] The present invention relates to a method of manufacturing an organic EL (electroluminescent) element, and an organic EL element manufactured by the method.

[0002] In recent years, development of an organic EL element (a luminous element having a structure including an anode and a cathode, and a light emitting layer composed of an organic matter sandwiched between the anode and the cathode) has increasingly proceeded to provide a self-luminescent type display as an alternative of a liquid crystal display. Materials for the light emitting layer of such an organic EL element include, for example, a low molecular weight organic material such as quinolinolatoaluminum complex (Alq3) and a high molecular weight organic material such as poly(paraphenylene-vinylene) (PPV).

[0003] A film of a light emitting layer composed of a low molecular weight organic material is formed by vapor deposition process, as is described in, for example, "Appl. Phys. Lett. 51(12), 21 September 1987 pp. 913". A film of a light emitting layer composed of a high molecular weight organic material is formed by coating process, as is described in, for example, "Appl. Phys. Lett. 71(1), 7 July 1997 pp. 34-".

[0004] In many cases, a hole transporting layer is provided between the light emitting layer and the anode of the organic EL element. A hole is injected from the anode to the hole transporting layer, and the hole transporting layer transports the hole to the light emitting layer. When the light emitting layer has a capability of transporting a hole, the hole transporting layer is not always provided. In some cases, a hole injecting layer is provided as a layer other than the hole transporting layer. When the light emitting layer is composed of a high molecular weight material such as PPV, a conductive polymer such as a polythiophene derivative or a polyaniline derivative is used as the hole transporting layer in many cases. When the light emitting layer is composed of a low molecular weight material such as Alq3, a phenylamine derivative or the like is used as the hole transporting layer in many cases.

[0005] For example, in an organic EL element for display, anodes are formed in individual pixels on a substrate, and a light emitting layer and a hole transporting layer must be placed on each anode. Accordingly, if the light emitting layer and the hole transporting layer can be placed by ink jet process, coating (application) and patterning can be performed concurrently to thereby yield a patterning with a high precision for a short time. Additionally, this process is also effective to cut wastes in material and to reduce manufacturing cost, since a minimum of material is enough to be used.

[0006] To place the light emitting layer and hole transporting layer by ink jet process, liquid materials must be used. When a high molecular weight material such as PPV is used as the material for light emitting layer, the

use of, for example, a solution of its precursor can place the light emitting layer by ink jet process. The placement of a light emitting layer composed of PPV high molecular weight material is described in, for example, Japanese Unexamined Patent Application Publication No. 11-40358, Japanese Unexamined Patent Application Publication No. 11-54270, and Japanese Unexamined Patent Application Publication No. 11-339957.

[0007] In the ink jet process, a region on which the light emitting layer and hole transporting layer are formed is surrounded with a barrier, and a liquid material is discharged toward the region surrounded with the barrier to thereby place the liquid material in the region. As the barrier, a two-layer structure barrier comprising a lower layer (substrate side) composed of an inorganic insulator such as silicon oxide, and an upper layer composed of an organic polymer such as polyimide is described in, for example, PCT International Publication No. WO99/48339.

[0008] Fig. 21 is a sectional view showing the aforementioned structure. Each of anodes 2 is formed in each pixel position on substrate 1, and lower barrier 31 composed of silicon oxide is formed so as to surround the periphery of each anode 2. Additionally, upper barrier 32 composed of polyimide is formed on lower barrier 31. Lower barrier 31 and upper barrier 32 are formed, for example, to a thickness (total thickness) of 1 to 3 μm by thin-film formation and patterning operations.

[0009] In this connection, PCT International Publication No. WO99/48339 also describes the liquid-repellent treatment of the surface of the upper layer of the barrier by plasma treatment.

[0010] However, in the barrier of two-layer structure in which the upper barrier is composed of polyimide, the thickness of the light emitting layer might become uneven in the vicinity of the barrier and at the center, from the points of the height of the barrier, and of the affinity for polyimide of a liquid (a liquid containing a material for the formation of light emitting layer) discharged by ink jet process. When the thickness of the light emitting layer becomes uneven, the light emission color or the amount of light emission becomes uneven or unstable in the pixel to thereby deteriorate luminous efficacy.

[0011] In a color display in which red, green and blue three color pixels are placed adjacent to one another, it is necessary to ensure that different liquids are placed separately in adjacent pixels and to avoid the liquid in each pixel from being contaminated by another liquid for the adjacent pixel. The barrier having the aforementioned structure is also susceptible to improvement in this point. In a contaminated pixel, purity of emitted light color is deteriorated.

[0012] In this connection, these problems can be improved also by the method described in PCT International Publication No. WO99/48339, but this method requires plasma treatment and is also susceptible to improvement in, for example, cost.

[0013] The present invention has been accomplished

focusing attention on these problems of the conventional technologies, and an object of the present invention is to ensure that a liquid is placed in a predetermined region (without placing the same in the adjacent region) to a uniform thickness in the region, when a light emitting layer or hole transporting layer constituting an organic EL element is placed by a liquid placing step such as ink jet process.

[0014] In order to solve the above problems, the present invention provides a method of manufacturing an organic EL element including a cathode, an anode, and one or more constitutive layers sandwiched between the cathode and anode, which constitutive layer includes at least a light emitting layer. The method includes the step of selectively placing a liquid containing a material for the formation of constitutive layer in a region for the formation of constitutive layer, using a pattern having an opening corresponding to the region for the formation of constitutive layer, in at least one constitutive layer, and, in the liquid placing step, an ultrathin organic film pattern having a surface being repellent to the liquid is formed as the pattern, using a compound having a functional group being bondable to the constitutive atom of a face, on which the film is formed, and a functional group being repellent to the liquid.

[0015] The liquid-repellency of the surface of the ultrathin organic film pattern is preferably such liquid-repellency that the contact angle of the liquid is 50° or more.

[0016] In the method according to the present invention, it is preferred that at least one constitutive layer is further subjected to the step of forming an ultrathin organic film on a face on which the constitutive layer is formed, which ultrathin organic film has a surface having affinity for the liquid, using a compound having a functional group being bondable to the constitutive atom of a face on which the film is formed, and a functional group having affinity for the liquid, and this step is between the ultrathin organic film pattern forming step and the liquid placing step.

[0017] The term "ultrathin film" as used in the present invention means a thin film having a thickness of about several nanometers (e.g., 3 nm or less). Such an ultrathin organic films includes, for example, a self-assembled film. The aforementioned ultrathin organic film pattern is preferably a pattern composed of a self-assembled film.

[0018] The term "self-assembled film" as used in the present invention means a monomolecular film which is obtained by allowing a compound having a straight-chain molecule and a functional group that can be combined with the constitutive atom of a face on which the film is formed and is bonded to the straight-chain molecule to become in the state of a gas or liquid and coexistent with the face on which the film is formed. In the monomolecular film, the functional group is adsorbed by the film-forming face and is bonded with the constitutive atom of the film-forming face, and the straight-chain

molecule is formed facing the outside. This monomolecular film is called as a self-assembled film, since it is formed by spontaneous chemical adsorption of the compound to the film-forming face.

[0019] In this connection, the self-assembled film is described in detail by A. Ulman in Chapter 3 of "An Introduction to Ultrathin Organic Film From Langmuir-Blodgett to Self-Assembly" (Academic Press Inc., Boston, 1991).

[0020] The liquid-repellent ultrathin organic film pattern includes a pattern composed of a self-assembled film which is formed by using a material having a fluoroalkyl group such as a fluoroalkylsilane. In this case, the face on which the film is formed must be converted into hydrophilic.

[0021] When a self-assembled film is formed on a hydrophilic film-forming face (a film-forming face on which a hydrophilic group such as hydroxyl group exists) using a fluoroalkylsilane, a siloxane bond is formed by dehydration reaction with the hydroxyl group of the film-forming face, and a fluoroalkyl group ($\text{CF}_3(\text{CF}_2)_n(\text{CH}_2)_m-$) is placed at the end of a straight-chain molecule, and the surface of the resulting self-assembled film becomes repellent to liquid (a property resistant to wetting with a liquid).

[0022] The ultrathin organic film forming step can be performed by the step of entirely forming an ultrathin organic film having a liquid-repellent surface using the compound, and the step of irradiating the ultrathin organic film with ultraviolet radiation via a photomask to thereby remove a portion corresponding to the constitutive layer forming region of the ultrathin organic film.

[0023] The lyophilic ultrathin organic film is preferably a self-assembled film composed of a material having an amino group or carboxyl group as a lyophilic functional group. When an amino group or carboxyl group is present on the surface, the film has a high affinity for, for example, water and alcohol which are generally used as a solvent in a material for the formation of hole transporting layer.

[0024] As the material for the formation of hole transporting layer, for example, a mixture of polyethylene dioxythiophene with poly(styrenesulfonic acid), or copper phthalocyanine is used. Accordingly, a self-assembled film formed by the use of an alkylsilane having an amino group or carboxyl group as a lyophilic functional group is preferably used as the lyophilic ultrathin organic film which is formed as an underlayer of the hole transporting layer. By this configuration, the adhesion of the material for the formation of hole transporting layer is improved, since the resulting self-assembled film has an amino group or carboxyl group on its surface.

[0025] As the material for the formation of light emitting layer, for example, polyfluorene-based polymer or poly(phenylene-vinylene)-based polymer is used. Accordingly, when the lyophilic ultrathin organic film is formed as an underlayer of the light emitting layer, a self-assembled film, which is formed by the use of an alkyl-

silane having, for example, an allyl group, vinyl group, phenyl group, or benzyl group as the lyophilic functional group, is preferably used as the lyophilic ultrathin organic film. By this configuration, the adhesion of the light emitting layer composed of a polyfluorene-based polymer or poly(phenylene-vinylene)-based polymer is improved, since the resulting self-assembled film has an allyl group, vinyl group, phenyl group, or benzyl group on its surface.

[0026] The present invention provides a method in which the liquid placing step in the invented method is performed by ink jet process. Specifically, when the organic EL element is manufactured as an element constituting a pixel of a color display in which red, green and blue three color pixels are placed adjacent to one another, the invented method is preferably employed when a liquid containing a material for the formation of light emitting layer and/or hole transporting layer is placed by ink jet process.

[0027] The present invention provides, in another aspect, an organic EL element which includes a cathode and an anode, and a light emitting layer, a hole injecting layer and/or a hole transporting layer sandwiched between the cathode and the anode, at least one of the light emitting layer and the hole injecting layer and/or the hole transporting layer is surrounded with a barrier, which barrier has a two-layer structure composed of a thin insulating film layer and an ultrathin organic film layer formed on the thin insulating film layer. The ultrathin organic film layer has a liquid-repellent surface and is formed by using a compound having a functional group being bondable to the constitutive atom of a face on which the film is formed, and a functional group being repellent to the liquid.

[0028] The thin insulating film constituting the barrier of this two-layer thin film preferably has a film thickness of 50 to 200 nm, and the ultrathin organic film layer preferably has a film thickness of 3 nm or less.

[0029] Embodiments of the present invention will now be described by way of further example only and with reference to the accompanying drawings, in which:-

Fig. 1 is a diagram showing a method according to the first embodiment of the present invention.

Fig. 2 is a diagram showing the method according to the first embodiment of the present invention.

Fig. 3 is a diagram showing the method according to the first embodiment of the present invention.

Fig. 4 is a diagram showing the method according to the first embodiment of the present invention.

Fig. 5 is a diagram showing the method according to the first embodiment of the present invention.

Fig. 6 is a diagram showing the method according to the first embodiment of the present invention.

Fig. 7 is a diagram showing the method according to the first embodiment of the present invention.

Fig. 8 is a diagram showing the method according to the first embodiment of the present invention.

Fig. 9 is a diagram showing a method according to the second embodiment of the present invention.

Fig. 10 is a diagram showing the method according to the second embodiment of the present invention.

Fig. 11 is a diagram showing the method according to the second embodiment of the present invention.

Fig. 12 is a diagram showing the method according to the second embodiment of the present invention.

Fig. 13 is a diagram showing the method according to the second embodiment of the present invention.

Fig. 14 is a diagram showing the method according to the second embodiment of the present invention.

Fig. 15 is a diagram showing a method according to the third embodiment of the present invention.

Fig. 16 is a diagram showing the method according to the third embodiment of the present invention.

Fig. 17 is a diagram showing the method according to the third embodiment of the present invention.

Fig. 18 is a diagram showing the method according to the third embodiment of the present invention.

Fig. 19 is a diagram showing the method according to the third embodiment of the present invention.

Fig. 20 is a diagram showing the method according to the third embodiment of the present invention.

Fig. 21 is a diagram showing a conventional step of placing a liquid.

[First Embodiment]

[0030] The first embodiment of the present invention will be illustrated with reference to Figs. 1 to 8. One embodiment of the present invention will be described herein, taking a display comprising, as pixels, organic EL elements as example. In each figure, A is a sectional view of one pixel, and B is a plan view thereof. This organic EL element includes two constitutive layers, i.e., a hole transporting layer and a light emitting layer, between an anode and a cathode.

[0031] Initially, ITO electrode (anode) 2 is formed in each pixel position on glass substrate 1, as shown in Fig. 1. On glass substrate 1, a semiconductor device for driving organic EL element, for example, has been formed in advance.

[0032] Next, a thin SiO₂ film is formed on all of glass substrate 1 by, for example, CVD process. Subsequently, a conventional patterning step including a photolithography step and an etching step is preformed to thereby form opening 3a in a region on which constitutive layer is formed (a predetermined region on ITO electrode 2) of the thin SiO₂ film. By this procedure, thin SiO₂ film pattern 3 is formed on the outermost surface of glass substrate 1. Fig. 2 shows this state. In the present embodiment, opening 3a is circular and the thin SiO₂ film has a thickness of 150 nm.

[0033] Next, self-assembled film 4 is formed on all of the faces (the top face of thin SiO₂ film pattern 3, the top face of ITO electrode 2 exposed to opening 3a, and the inner wall of opening 3a) of glass substrate 1 using

heptadecafluorotetrahydrodecyltrimethoxysilane. Fluorid-repellent fluoroalkyl groups are present on all of the surface of self-assembled film 4. Here, self-assembled film 4 having a thickness of about 1 nm is formed by allowing glass substrate 1 in the state shown in Fig. 2 to stand in the atmosphere of heptadecafluorotetrahydrodecyltrimethoxysilane for 96 hours. Fig. 3 shows this state.

[0034] In this state, concave 4a having self-assembled film 4 on its outermost surface exists on glass substrate 1. The shape of opening of concave 4a is the same, circular, as in opening 3a of thin SiO₂ film pattern 3, and the radius thereof is smaller than that of opening 3a by a factor of the thickness of self-assembled film 4.

[0035] Next, self-assembled film 4 on glass substrate 1 is irradiated with ultraviolet radiation (wavelength: 172 nm) via photomask 5 having light transmitting part 5a corresponding to the circular opening of concave 4a, as shown in Fig. 4. By this procedure, self-assembled film 4 in portions exposed to ultraviolet radiation, i.e., the top face of ITO electrode 2 and the inner wall of opening 3a is removed, and self-assembled film 4 remains only on the top face of thin SiO₂ film pattern 3.

[0036] Thus, ultrathin organic film pattern 41 having a liquid-repellent surface is formed on thin SiO₂ film pattern 3. Opening 4b of ultrathin organic film pattern 41 is placed so that its inner wall is located at the same location or somewhat outside of the inner wall of opening 3a of thin SiO₂ film pattern 3.

[0037] In this state, as shown in Fig. 5, liquid 6 containing a material for the formation of hole transporting layer is discharged toward opening 4b of ultrathin organic film pattern 41 from above by ink jet process. In this embodiment, an aqueous solution of polyethylene dioxathiophene and poly(styrenesulfonic acid) as materials for the formation of hole transporting layer is used as liquid 6.

[0038] The surface of ultrathin organic film pattern 41 becomes repellent to liquid, and discharged liquid 6 does not remain on the top face of ultrathin organic film pattern 41 and all of discharged liquid 6 enters opening 3a. When liquid 6 overflows opening 3a, the top face of liquid 6 is raised over opening 4b of ultrathin organic film pattern 41, as shown by a chain double-dashed line in Fig. 5. Accordingly, liquid 6 discharged toward one opening 4b does never enter an adjacent opening 4b.

[0039] Next, glass substrate 1 is heated at a predetermined temperature to thereby remove the solvent from discharged liquid 6. By this procedure, hole transporting layer 61 composed of a mixture of polyethylene dioxathiophene and poly(styrenesulfonic acid) is formed in opening 3a of thin SiO₂ film pattern 3. Fig. 6 shows this state. In this embodiment, hole transporting layer 61 has a thickness of 60 nm.

[0040] Next, in this state, liquid 7 containing a material for the formation of light emitting layer is discharged toward opening 4b of ultrathin organic film pattern 41 from above by ink jet process, as shown in Fig. 6. A liquid, a

solution of poly(paraphenylene-vinylene) (a material for the formation of light emitting layer) in xylene, is used as liquid 7 containing a material for the formation of light emitting layer.

[0041] As is described above, the surface of ultrathin organic film pattern 41 becomes repellent to liquid also in this case, and discharged liquid 7 does not remain on the top face of ultrathin organic film pattern 41 but all of which enters opening 3a. Accordingly, liquid 7 discharged toward one opening 4b does never enter an adjacent opening 4b.

[0042] Next, glass substrate 1 is heated at a predetermined temperature to thereby remove the solvent from discharged liquid 7. By this procedure, light emitting layer 71 composed of, for example, a polyfluorene-based polymer is formed in opening 3a of thin SiO₂ film pattern 3. Fig. 7 shows this state. In this embodiment, light transmitting layer 71 has a thickness of 80 nm.

[0043] Next, in this state, cathode 8 is formed in a position over ITO electrode 2 of glass substrate 1. Cathode 8 is formed from a material that has an appropriate work function and is selected depending on the light emitting layer. In this embodiment, cathode 8 is formed as a two-layer structure cathode layer by forming a thin calcium film having a thickness of 10 nm by vapor deposition process, and further forming a thin aluminium film having a thickness of 400 nm on the thin calcium film by vapor deposition process. A protective film is formed or a sealing glass is bonded on cathode 8 according to necessity.

[0044] Thus, an organic EL element having hole transporting layer 61 and light emitting layer 71 between ITO electrode (anode) 2 and cathode 8 is formed in each pixel position of the display. In this organic EL element, light emitting layer 71 and hole transporting layer 61 are surrounded with a two-layer structure barrier composed of thin SiO₂ film pattern (thin insulating film layer) 3 and ultrathin organic film pattern (ultrathin organic film layer having a liquid-repellent surface) 41. Thin SiO₂ film pattern 3 is formed herein so as to prevent electric leak between ITO electrode (anode) 2 and cathode 8.

[0045] According to the method of the present embodiment, liquids 6 and 7 containing materials for the formation of hole transporting layer 61 and light emitting layer 71 are discharged, by ink jet process, toward opening 4b of ultrathin organic film pattern 41 from above ultrathin organic film pattern 41 having a liquid-repellent surface. Therefore, liquids 6 and 7 discharged toward one opening 4b are prevented from entering an adjacent opening 4b. Accordingly, by producing organic EL elements of a color display in which red, green and blue three color pixels are placed adjacent to one another according to the method of the present embodiment, purity of light color emitted from a pixel of each color can be increased.

[0046] Separately, in a conventional liquid-repellent pattern composed of plasma-treated polyimide, discharged liquids may exist as convex or concave droplets

in the opening of the liquid-repellent pattern, since the film thickness is on the order of micrometers and the surface condition cannot be significantly controlled in plasma treatment. The convex or concave droplets have difference in height on the order of micrometers corresponding to the film thickness of the liquid-repellent pattern. Specifically, the droplets may have uneven height in one opening 3a. Additionally, the droplets may have different shapes in different plural openings in some cases.

[0047] Contrary to this, ultrathin organic film pattern 41 according to the present embodiment is very thin of about 1 nm, and has an excellent repellency to liquid, and the discharged liquid does never exist as a convex or concave droplet in opening 4b of ultrathin organic film pattern 41, but is in the state that its top face is raised over opening 4b. As a result, the intra-opening 3a uniformity and inter-opening uniformity of the film thickness of hole transporting layer 61 and light emitting layer 71 can be increased, as compared with the conventional liquid-repellent pattern.

[Second Embodiment]

[0048] The second embodiment of the present invention will be described with reference to Figs. 9 to 14. One embodiment of the present invention is described herein, taking a display having organic EL elements as pixels as example. In each figure, A is a sectional view of one pixel, and B is a plan view thereof. This organic EL element includes two constitutive layers, i.e., a hole transporting layer and a light emitting layer, between an anode and a cathode.

[0049] Initially, ITO electrode (anode) 2 is formed in each pixel position on glass substrate 1, thin SiO₂ film pattern 3 having opening 3a is formed thereon, and ultrathin organic film pattern 41 having a liquid-repellent surface is formed on thin SiO₂ film pattern 3, by performing the steps shown in Figs. 1 to 4 in the same manner as in the first embodiment. Fig. 9 shows this state.

[0050] Next, self-assembled film 9 is formed on the top face of ITO electrode 2 exposed to opening 3a on glass substrate 1, using aminopropyltriethoxysilane. Fig. 10 shows this state. Lyophilic amino groups are present on all of the surface of self-assembled film 9. In this embodiment, self-assembled film 9 having a thickness of about 0.5 nm is formed by dipping glass substrate 1 in the state shown in Fig. 9 in a methanol 1% solution containing aminopropyltriethoxysilane, and rinsing the glass substrate with methanol and with water.

[0051] Next, in this state, the same liquid 6 (a liquid containing a material for the formation of hole transporting layer) as in the first embodiment is discharged toward opening 4b of ultrathin organic film pattern 41 from above by ink jet process. The surface of ultrathin organic film pattern 41 becomes repellent to liquid, and discharged liquid 6 does not remain on the top face of ultrathin organic film pattern 41 but all of discharged liquid

6 enters opening 3a. Accordingly, liquid 6 discharged toward one opening 4b does never enter an adjacent opening 4b.

[0052] Additionally, self-assembled film (ultrathin organic film) 9 having amino groups on its surface is formed on the top face of ITO electrode 2, and discharged liquid 6 is placed dense in the state that it uniformly spreads over self-assembled film 9.

[0053] Next, glass substrate 1 is heated at a predetermined temperature to thereby remove the solvent from discharged liquid 6. By this procedure, hole transporting layer 61 composed of a mixture of polyethylene dioxythiophene and poly(styrenesulfonic acid) is formed in opening 3a of thin SiO₂ film pattern 3. Fig. 11 shows this state. Hole transporting layer 61 has a thickness of 60 nm also in this embodiment.

[0054] Next, glass substrate 1 in this state is dipped in a methanol 1% solution containing allyltriethoxysilane, and is then rinsed with methanol and with water to thereby form self-assembled film 10 having a thickness of about 0.4 nm on the top surface of hole transporting layer 61 exposed to opening 3a. Allyl groups are present on all of the surface of self-assembled film 10. Fig. 12 shows this state.

[0055] Next, the same liquid 7 (a liquid containing a material for the formation of light emitting layer) as in the first embodiment is discharged toward opening 4b of ultrathin organic film pattern 41 from above by ink jet process, as shown in Fig. 12. As described above, the surface of ultrathin organic film pattern 41 becomes repellent to liquid also in this case, and discharged liquid 7 does not remain on the top face of ultrathin organic film pattern 41, but all of which enters opening 3a. Accordingly, liquid 7 discharged toward one opening 4b does never enter an adjacent opening 4b.

[0056] Additionally, self-assembled film (an ultrathin organic film having a lyophilic surface) 10 having allyl groups lyophilic to liquid 7 on its surface (a solution of poly(para-phenylene-vinylene) in xylene) is formed on the top face of hole transporting layer 61, and discharged liquid 7 is placed in the state that it uniformly spreads over self-assembled film 10.

[0057] Next, glass substrate 1 is heated at a predetermined temperature to thereby remove the solvent from discharged liquid 7. By this procedure, light emitting layer 71 composed of poly(para-phenylene-vinylene) is formed in opening 3a of thin SiO₂ film pattern 3. Fig. 13 shows this state.

[0058] Next, in this state, cathode 8 is formed in a position over ITO electrode 2 of glass substrate 1. Fig. 14 shows this state. A two-layer structure cathode layer composed of a thin calcium film having a thickness of 10 nm and a thin aluminium film having a thickness of 400 nm is also formed in this embodiment as in the first embodiment. A protective film is formed or a sealing glass is bonded on cathode 8 according to necessity.

[0059] Thus, an organic EL element having hole transporting layer 61 and light emitting layer 71 between

ITO electrode (anode) 2 and cathode 8 is formed in each pixel position of the display. This organic EL element includes self-assembled films 9 and 10 between ITO electrode 2 and hole transporting layer 61 and between hole transporting layer 61 and light emitting layer 71. These self-assembled films 9 and 10 are thin in film thickness and have an opening in which the hole can easily move and they do not significantly deteriorate the performances of the organic EL element.

[0060] Additionally, in this organic EL element, light emitting layer 71 and hole transporting layer 61 are surrounded with a two-layer structure barrier composed of thin SiO₂ film pattern (thin insulating film layer) 3 and ultrathin organic film pattern (ultrathin organic film layer having a liquid-repellent surface) 41.

[0061] According to the method of the present embodiment, the effect of increasing the durability of the organic EL element can be obtained, in addition to the effects as in the first embodiment, since the presence of self-assembled films 9 and 10 increases adhesion between ITO electrode 2 and hole transporting layer 61 and adhesion between hole transporting layer 61 and light emitting layer 71. Additionally, the uniformity in film thickness of hole transporting layer 61 and of light emitting layer 71 in opening 3a of thin SiO₂ film pattern 3 can be further increased in comparison with the organic EL element obtained in the first embodiment.

[Third Embodiment]

[0062] The third embodiment of the present invention will be described below with reference to Figs. 15 to 20. One embodiment in which an organic EL element is applied to a surface light source device such as back light will be illustrated herein. In each figure, A is a plan view, and B is a sectional view of A along with the lines A-A. This organic EL element includes two layers, i.e., a hole transporting layer and a light emitting layer, as constitutive layers between a cathode and an anode.

[0063] Initially, ITO electrode (anode) 2 in a predetermined shape is formed on glass substrate 1, as shown in Fig. 15. ITO electrode 2 is composed of rectangular sandwiching part 21 for sandwiching the constitutive layers and terminal part 22 protruding from sandwiching part 21. ITO electrode 2 is formed by performing a conventional patterning step including a photolithography step and an etching step, after the formation of the thin ITO film by, for example, sputtering process. In this embodiment, ITO electrode 2 has a thickness of 150 nm.

[0064] Next, self-assembled film 4 is formed on all of the faces of glass substrate 1 using heptadecafluorotetrahydrodecyltriethoxysilane, as shown in Fig. 16. Fluid-repellent fluoroalkyl groups are present on all of the surface of self-assembled film 4. Glass substrate 1 in the state shown in Fig. 15 is allowed to stand in the atmosphere of heptadecafluorotetrahydrodecyltriethoxysilane for 96 hours to thereby form self-assembled film 4 having a film thickness of about 1 nm.

[0065] Next, self-assembled film 4 on glass substrate 1 is irradiated with ultraviolet radiation (wavelength: 172 nm) via photomask 5 having a light transmitting part corresponding to the region for the formation of constitutive layer (a rectangular region which is of a size larger than that of sandwiching part 21 of ITO electrode 2). By this procedure, the self-assembled film in portions exposed to ultraviolet radiation is removed to thereby form ultrathin organic film pattern 41 that has opening 4b corresponding to the region for the formation of constitutive layer and has a liquid-repellent surface, as shown in Fig. 17.

[0066] In this state, an aqueous solution of a mixture (a material for the formation of hole transporting layer) of polyethylene dioxythiophene and poly(styrenesulfonic acid) is applied on the top face of glass substrate 1 by spin coating process. In this procedure, the surface of ultrathin organic film pattern 41 becomes repellent to liquid, and the liquid does not remain on the top face of ultrathin organic film pattern 41 but enters opening 4b alone and adheres onto ITO electrode 2 in opening 4b.

[0067] Next, glass substrate 1 is heated at a predetermined temperature to dry the film of the applied liquid to thereby form hole transporting layer 61 on ITO electrode 2. Fig. 18 shows this state. In this embodiment, hole transporting layer 61 has a thickness of 60 nm.

[0068] Next, a liquid, a solution of poly(para-phenylene-vinylene) (a material for the formation of light emitting layer) in xylene, is applied onto the top face of glass substrate 1 by spin coating process. Also in this procedure, the liquid is rejected by ultrathin organic film pattern 41 having a liquid-repellent surface, and enters opening 4b alone and adheres onto hole transporting layer 61 in opening 4b. Next, glass substrate 1 is heated at a predetermined temperature to dry the film of the applied liquid to thereby form light emitting layer 71 on hole transporting layer 61. Fig. 19 shows this state. In this embodiment, light transmitting layer 71 has a thickness of 80 nm.

[0069] Next, cathode 8 is formed on light emitting layer 71. Cathode 8 in this embodiment is also composed of rectangular sandwiching part 81 for sandwiching the constitutive layers, and terminal part 82 protruding from sandwiching part 81, which terminal part 82 is placed in a position in the same side of that of terminal part 22 of anode 2 but not overlapping the same. A two-layer structure anode layer composed of a thin calcium film having a thickness of 10 nm and a thin aluminium film having a thickness of 400 nm is also formed in this embodiment in the same manner as in the first embodiment.

[0070] Next, ultrathin organic film pattern 41 is removed to allow terminal part 22 of anode 2 to expose itself, and then a protective film is formed or a sealing glass is bonded on cathode 8 according to necessity.

[0071] Thus, an organic EL element having hole transporting layer 61 and light emitting layer 71 between ITO electrode (anode) 2 and cathode 8 is formed as a surface light source device.

[0072] According to the method of the present embodiment, when each liquid containing a material for the formation of hole transporting layer 61 or light emitting layer 71 is applied by spin coating process, the portions other than the regions for the formation of the two layers 61 and 71 are covered with ultrathin organic film pattern 41 having a liquid-repellent surface, and each liquid is prevented from adhering to, for example, the reverse face of glass substrate 1.

[0073] In this connection, in the method of manufacturing an organic EL element for surface light source device, a process (dipping process) in which the top face of glass substrate 1 is dipped in the liquid can also be advantageously employed as the process for applying each liquid containing a material for the formation of hole transporting layer 61 or light emitting layer 71, in addition to the spin coating process.

[0074] Separately, in the method of manufacturing an organic EL element for display pixel, spin coating process or dipping process can also be employed as the process for applying the liquid containing a material for the formation of hole transporting layer 61. In the method of manufacturing an organic EL element for display pixel, spin coating process or dipping process can also be employed as the process for applying the liquid containing a material for the formation of light emitting layer 71, except when the display is a color display in which red, green and blue three color pixels are placed adjacent to one another.

[0075] Additionally, the lyophilic ultrathin organic film (self-assembled films 9 and 10) may be formed by a process in which glass substrate 1 is dipped in a solution of an alkylsilane having an amino group or carboxyl group in a solvent such as methanol or ethanol.

[0076] In the first embodiment and second embodiment, thin insulating film layer 3 can also be formed by the following method. Initially, glass substrate 1 in the state shown in Fig. 1 is allowed to stand in the atmosphere of heptadecafluorotetrahydrodecyltriethoxysilane for 96 hours to thereby form a self-assembled film having a liquid-repellent surface. Next, this self-assembled film is irradiated with ultraviolet radiation (wavelength: 172 nm) via a photomask having a light shielding part corresponding to the region for the formation of constitutive layers, and a light transmitting part corresponding to the other portions. By this procedure, the self-assembled film only remains on the region for the formation of constitutive layer on ITO electrode 2.

[0077] Next, a solution of peroxy polysilazane in a solvent is applied onto the surface of the glass substrate in this state. By this procedure, this solution does not remain on the self-assembled film having a liquid-repellent surface and is placed in the opening (a portion other than the region for the formation of constitutive layers on ITO electrode 2) of the self-assembled film. Next, the glass substrate in this state is heated at a predetermined temperature to thereby form a thin insulating film mainly containing silicon oxide in the aforementioned portion.

[0078] Next, the surface of the glass substrate in this state is irradiated with ultraviolet radiation (wavelength: 172 nm) to thereby remove the self-assembled film remained on the region for the formation of constitutive layers on ITO electrode 2. As a result, thin insulating film layer 3 having opening 3a in the region for the formation of constitutive layers is formed on ITO electrode 2, as shown in Fig. 2.

[0079] As described above, the invented method of manufacturing an organic EL element can ensure that a liquid containing a material for the formation of constitutive layer (light emitting layer or hole transporting layer) (without being placed in the adjacent region) is placed in the region for the formation of constitutive layers with a uniform thickness in the region. Additionally, the invented method can suppress cost, in comparison with a method using plasma treatment.

[0080] In particular, by applying the invented method to a method of producing an organic EL element for a color display pixel, in which a liquid containing a material for the formation of light emitting layer is placed by ink jet process, and red, green and blue three color pixels are placed adjacent to one another, the purity of light color emitted from a pixel of each color can be increased and luminous efficacy can be increased.

Claims

1. A method of manufacturing an organic EL element including a cathode, an anode, and one or more constitutive layers sandwiched between said cathode and anode, said constitutive layer including at least a light emitting layer, wherein

said method comprises the step of selectively placing a liquid containing a material for the formation of constitutive layer in a region for the formation of constitutive layer, using a pattern having an opening corresponding to the region for the formation of constitutive layer, in at least one constitutive layer, and wherein in said liquid placing step, an ultrathin organic film pattern having a surface being repellent to said liquid is formed as said pattern, using a compound having a functional group being bondable to the constitutive atom of a face, on which the film is formed, and a functional group being repellent to said liquid.

2. A method of manufacturing an organic EL element according to claim 1, wherein at least one constitutive layer is subjected to the step of forming an ultrathin organic film on a face on which the constitutive layer is formed, said ultrathin organic film having a surface having affinity for said liquid, using a compound having a functional group being bondable to the constitutive atom of a face on which the

film is formed, and a functional group having affinity for said liquid, said step being between said ultrathin organic film pattern forming step and said liquid placing step.

3. A method of manufacturing an organic EL element according to claim 1 or 2, wherein said ultrathin organic film pattern is a pattern composed of a self-assembled film. 5
4. A method of manufacturing an organic EL element according to claim 1, wherein said liquid-repellent ultrathin organic film pattern is a pattern composed of a self-assembled film comprising a material having a fluoroalkyl group. 10
5. A method of manufacturing an organic EL element according to claim 1, wherein said ultrathin organic film forming step is performed by the step of forming an ultrathin organic film having a liquid-repellent surface using said compound, and the step of irradiating said ultrathin organic film with ultraviolet radiation via a photomask to thereby remove a portion corresponding to the region of said ultrathin organic film for the formation of constitutive layer. 15
6. A method of manufacturing an organic EL element according to claim 2, wherein said ultrathin organic film having affinity for liquid is a self-assembled film having an amino group or carboxyl group as the lyophilic functional group. 20
7. A method of manufacturing an organic EL element according to any one of claims 1 to 6, wherein said liquid placing step is performed by ink jet process. 25
8. An organic EL element comprising a cathode and an anode, and a light emitting layer, a hole injecting layer and/or a hole transporting layer sandwiched between said cathode and said anode, wherein 30

at least one of said light emitting layer and said hole injecting layer and/or said hole transporting layer is surrounded with a barrier, said barrier having a two-layer structure composed of a thin insulating film layer and an ultrathin organic film layer formed on said thin insulating film layer, said ultrathin organic film layer having a liquid-repellent surface and being formed by using a compound having a functional group being bondable to the constitutive atom of a face on which the film is formed, and a functional group being repellent to said liquid. 45

Patentansprüche

1. Verfahren zur Herstellung eines organischen 55

EL-Elements, enthaltend eine Kathode, eine Anode, und eine oder mehrere Teilschichten, die zwischen der Kathode und Anode liegen, wobei die Teilschicht mindestens eine Lichtemissionsschicht enthält, wobei

das Verfahren den Schritt des selektiven Anordnens einer Flüssigkeit, die ein Material zur Bildung einer Teilschicht enthält, in einem Bereich zur Bildung einer Teilschicht, unter Verwendung eines Musters mit einer Öffnung, die dem Bereich für die Bildung der Teilschicht entspricht, in mindestens einer Teilschicht umfasst, und wobei

in dem Schritt zum Anordnen der Flüssigkeit als Muster ein ultradünnes organisches Filmmuster mit einer Oberfläche, die für die Flüssigkeit abweisend ist, unter Verwendung einer Verbindung mit einer funktionellen Gruppe, die an das konstitutive Atom einer Fläche binden kann, auf der der Film gebildet wird, und einer funktionellen Gruppe, die für die Flüssigkeit abweisend ist, gebildet wird.

2. Verfahren zur Herstellung eines organischen EL-Elements nach Anspruch 1, wobei mindestens eine Teilschicht dem Schritt zur Bildung eines ultradünnen organischen Films auf einer Fläche, auf der die Teilschicht gebildet wird, unterzogen wird, wobei der ultradünne organische Film eine Oberfläche mit Affinität für die Flüssigkeit hat, unter Verwendung einer Verbindung mit einer funktionellen Gruppe, die an das konstitutive Atom einer Fläche binden kann, auf der der Film gebildet wird, und einer funktionellen Gruppe, die Affinität für die Flüssigkeit hat, wobei der Schritt zwischen dem Schritt zur Bildung des ultradünnen organischen Filmmusters und dem Schritt zum Anordnen der Flüssigkeit erfolgt.
3. Verfahren zur Herstellung eines organischen EL-Elements nach Anspruch 1 oder 2, wobei das ultradünne organische Filmmuster ein Muster ist, das aus einem selbstaggregierenden Film besteht.
4. Verfahren zur Herstellung eines organischen EL-Elements nach Anspruch 1, wobei die Flüssigkeit abweisende ultradünne organische Filmmuster ein Muster ist, das aus einem selbstaggregierenden Film besteht, der ein Material mit einer Fluoroalkylgruppe umfasst.
5. Verfahren zur Herstellung eines organischen EL-Elements nach Anspruch 1, wobei der Schritt zur Bildung des ultradünnen organischen Films durch den Schritt zur Bildung eines ultradünnen organischen Films mit einer Flüssigkeit abweisenden

Oberfläche unter Verwendung der Verbindung, und den Schritt zum Bestrahlen des ultradünnen organischen Films mit Ultraviolettstrahlen durch eine Fotomaske, um **dadurch** einen Teil zu entfernen, der dem Bereich des ultradünnen organischen Films zur Bildung der Teilschicht entspricht, ausgeführt wird.

6. Verfahren zur Herstellung eines organischen EL-Elements nach Anspruch 2, wobei der ultradünne organische Film mit Affinität für die Flüssigkeit ein selbstaggregierender Film mit einer Aminogruppe oder Carboxylgruppe als lyophile funktionelle Gruppe ist.
7. Verfahren zur Herstellung eines organischen EL-Elements nach einem der Ansprüche 1 bis 6, wobei der Schritt zum Anordnen der Flüssigkeit durch ein Tintenstrahlverfahren ausgeführt wird.
8. Organisches EL-Element, umfassend eine Kathode und eine Anode, und eine Lichtemissionsschicht, eine Lochinjektionsschicht und/oder eine Lochtransportschicht, die zwischen der Kathode und der Anode liegen, wobei
 zumindest eine von der Lichtemissionsschicht und der Lochinjektionsschicht und/oder Lochtransportschicht von einer Sperrschicht umgeben ist, wobei die Sperrschicht eine zweilagige Struktur hat, die aus einer dünnen isolierenden Filmschicht und einer ultradünnen organischen Filmschicht, die auf der dünnen isolierenden Filmschicht gebildet ist, besteht,
 wobei die ultradünne organische Filmschicht eine Flüssigkeit abweisende Oberfläche hat und unter Verwendung einer Verbindung mit einer funktionellen Gruppe, die an das konstitutive Atom einer Fläche binden kann, auf der der Film gebildet wird, und einer funktionellen Gruppe, die für die Flüssigkeit abweisend ist, gebildet wird.

Revendications

1. Procédé de fabrication d'un élément électroluminescent comprenant une cathode, une anode, et une ou plusieurs couches constitutives prises en sandwich entre ladite cathode et ladite anode, ladite couche constitutive comprenant au moins une couche d'émission de lumière,
 ledit procédé comprenant l'étape consistant à sélectivement placer un liquide contenant une matière pour la formation d'une couche constitutive dans une zone pour la formation d'une couche constitutive, en utilisant une configuration avec une ouverture correspondant à la zone pour la formation de la couche constitutive, dans au moins une couche constitutive, et

au cours de ladite étape consistant à mettre en place le liquide, une configuration de pellicule organique ultramince ayant une surface hydrophobe par rapport audit liquide étant formée en tant que ladite configuration, en utilisant un composé avec un groupe fonctionnel pouvant être combiné avec l'atome constitutif d'une face sur laquelle la pellicule est formée, et un groupe fonctionnel hydrophobe par rapport audit liquide.

2. Procédé de fabrication d'un élément électroluminescent selon la revendication 1, où au moins une couche constitutive est soumise à l'étape de formation d'une pellicule organique ultramince sur une face sur laquelle la couche constitutive est formée, ladite pellicule organique ultramince possédant une surface en affinité avec ledit liquide, en utilisant un composé avec un groupe fonctionnel pouvant être combiné avec l'atome constitutif d'une face sur laquelle la pellicule est formée, et un groupe fonctionnel en affinité avec ledit liquide, ladite étape se situant entre ladite étape de formation de la configuration de pellicule organique ultramince et ladite étape de mise en place du liquide.
3. Procédé de fabrication d'un élément électroluminescent organique selon les revendications 1 ou 2, où ladite configuration de pellicule organique ultramince est une configuration se composant d'une pellicule à auto-assemblage.
4. Procédé de fabrication d'un élément électroluminescent organique selon la revendication 1, où ladite configuration de pellicule organique ultramince est une configuration se composant d'une pellicule à auto-assemblage comprenant une matière avec un groupe fluoralkyle.
5. Procédé de fabrication d'un élément électroluminescent organique selon la revendication 1, où ladite étape de formation d'une pellicule organique ultramince est réalisée par l'étape consistant à former une pellicule organique ultramince ayant une surface hydrophobe en utilisant ledit composé, et l'étape consistant à irradier ladite pellicule ultramince avec des radiations ultraviolettes via un photomasque afin d'enlever de la sorte une partie correspondant à la zone de ladite pellicule organique ultramince pour la formation d'une couche constitutive.
6. Procédé de fabrication d'un élément électroluminescent organique selon la revendication 2, où ladite pellicule organique ultramince en affinité avec du liquide est une pellicule à auto-assemblage avec un groupe aminé et un groupe carboxyle en tant que groupe fonctionnel lyophile.
7. Procédé de fabrication d'un élément électrolumi-

nescent organique selon l'une quelconque des revendications 1 à 6, où ladite étape de mise en place d'un liquide est réalisée grâce à un procédé de jet d'encre.

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8. Élément électroluminescent organique comprenant une cathode et une anode, et une couche d'émission de lumière, une couche d'injection de trous et/ou une couche de transport de trous prise en sandwich entre ladite cathode et ladite anode, 10
au moins l'une parmi ladite couche d'émission de lumière et ladite couche d'injection de trous et/ou couche de transport de trous étant entourée d'une couche de jonction, 15
ladite couche de jonction présentant une structure à deux couches se composant d'une mince couche de pellicule isolante et d'une couche de pellicule organique ultramince formée sur ladite mince couche de pellicule isolante, ladite couche de pellicule organique ultramince ayant une surface hydrophobe 20
et étant formée en utilisant un composé avec un groupe fonctionnel pouvant être combiné avec l'atome constitutif d'une face sur laquelle la pellicule est formée, et un groupe fonctionnel qui est hydrophobe par rapport audit liquide. 25

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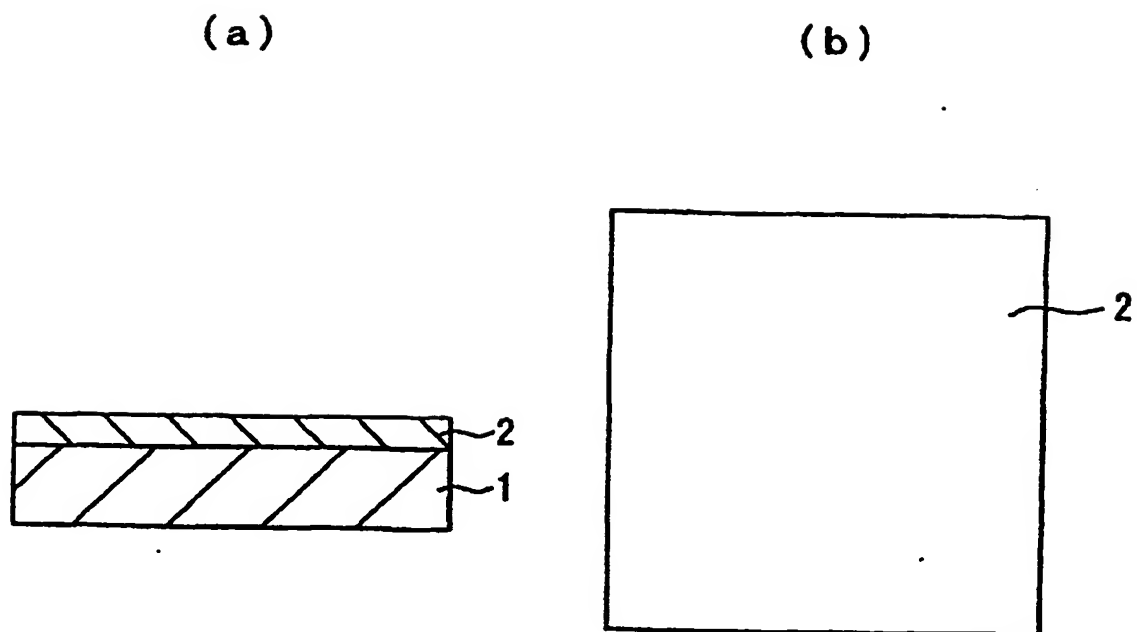
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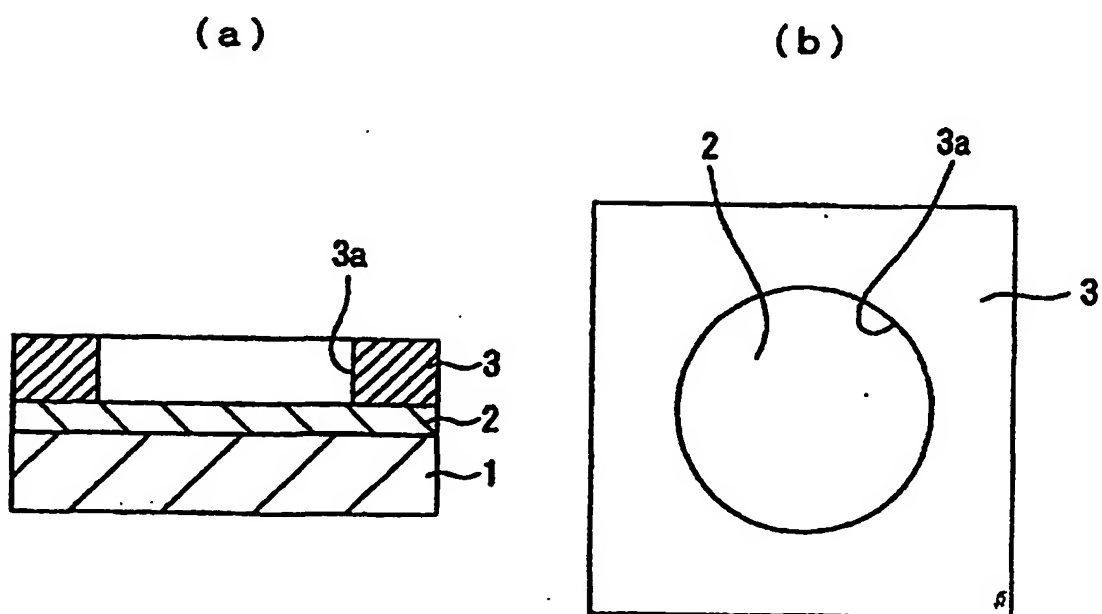
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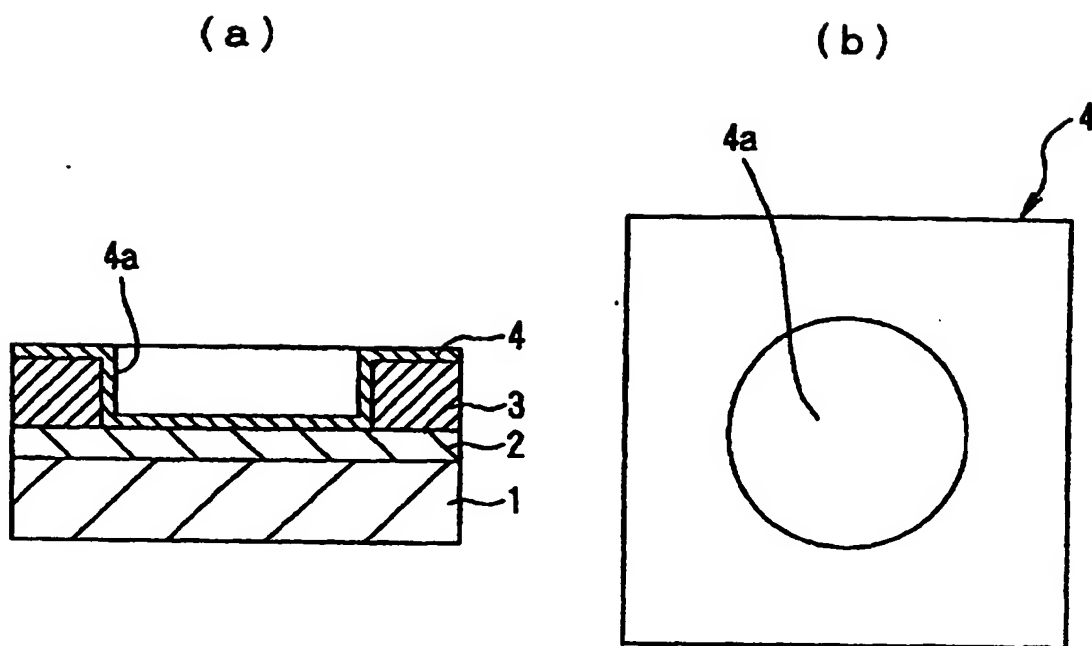
[FIG. 1]



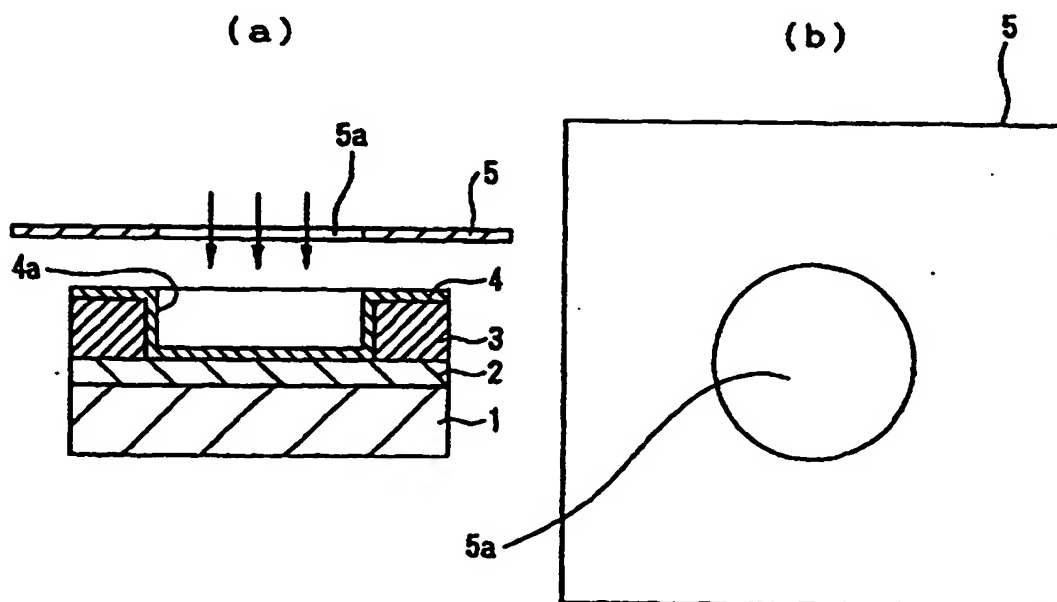
[FIG. 2]



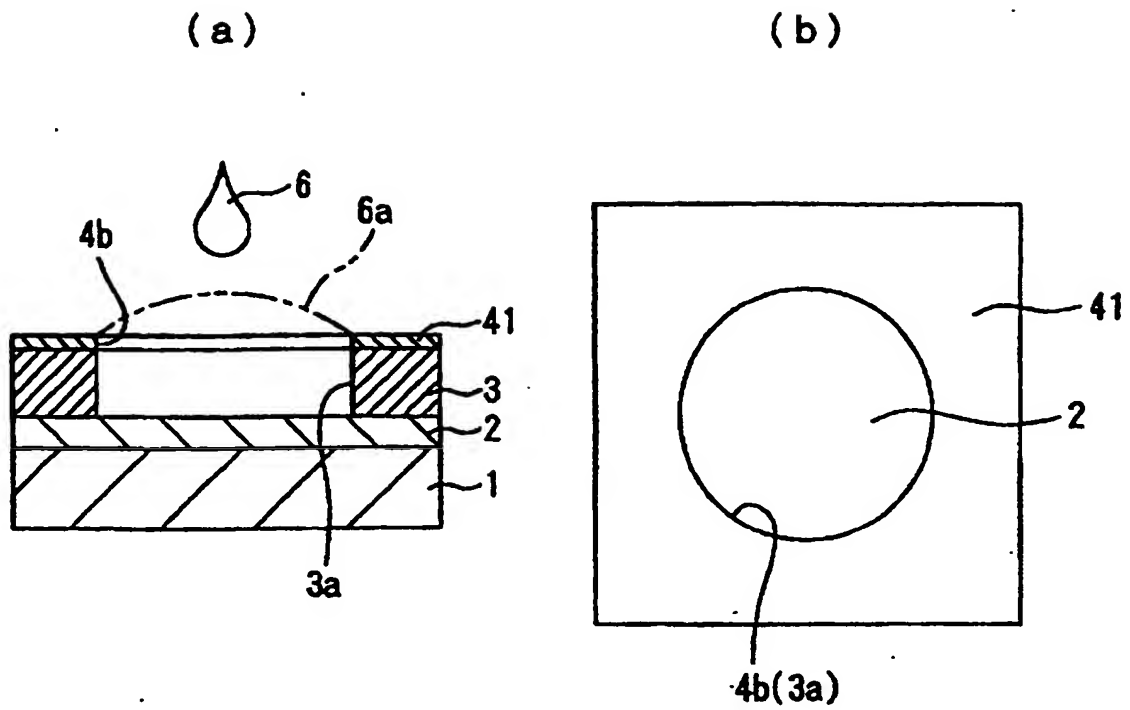
[FIG. 3]



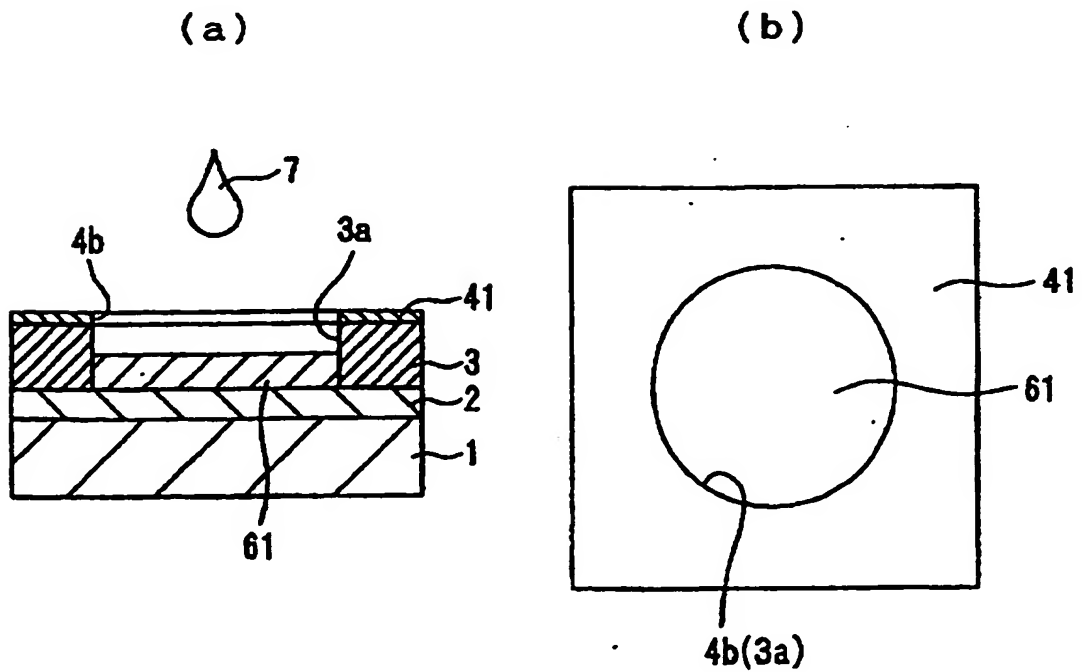
[FIG. 4]



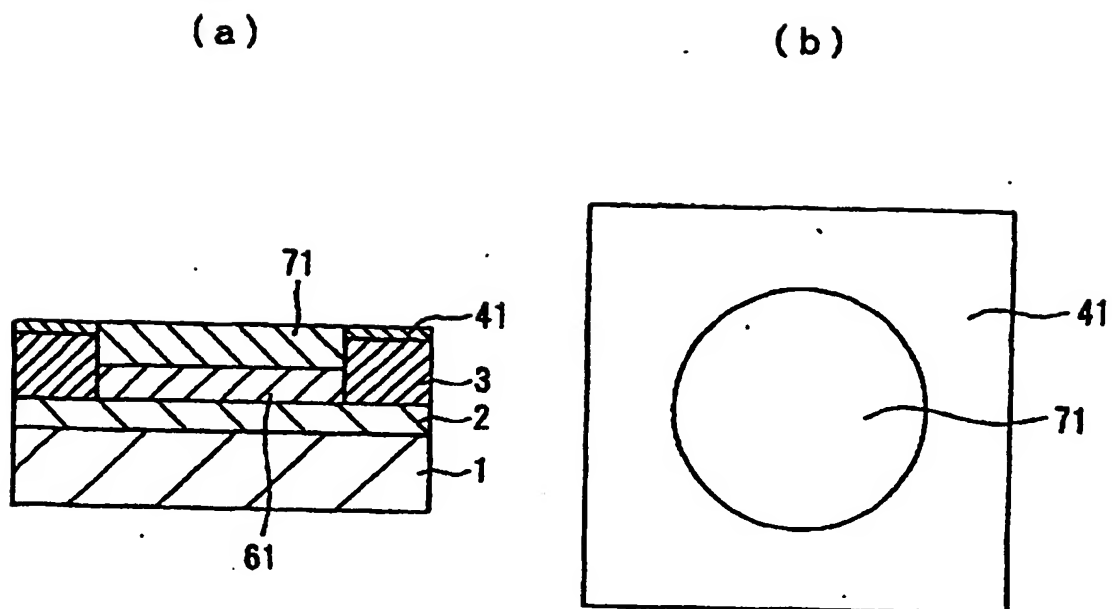
[FIG. 5]



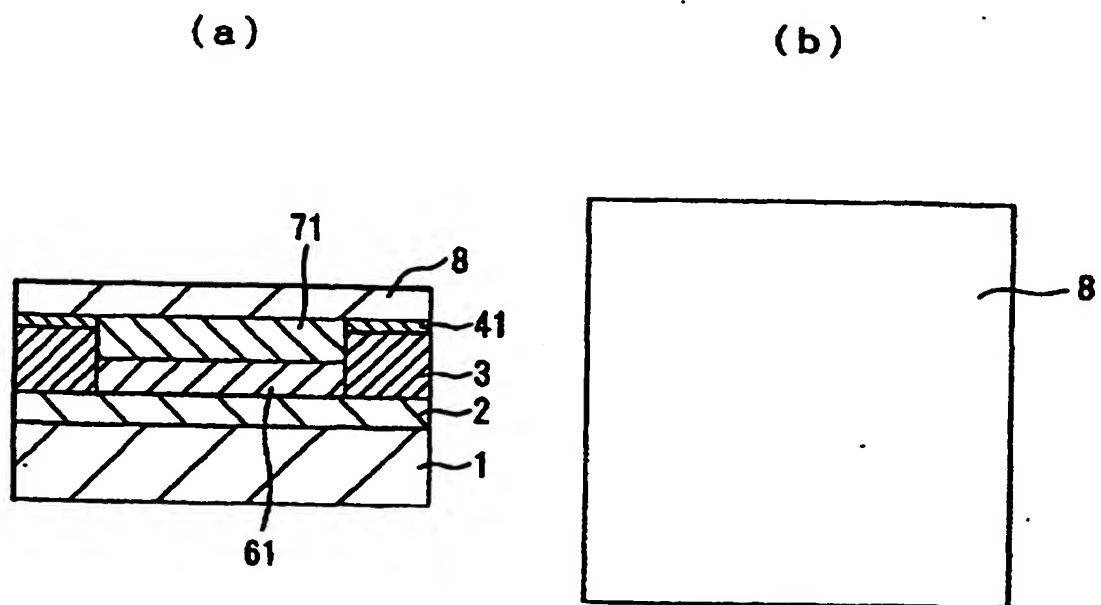
[FIG. 6]



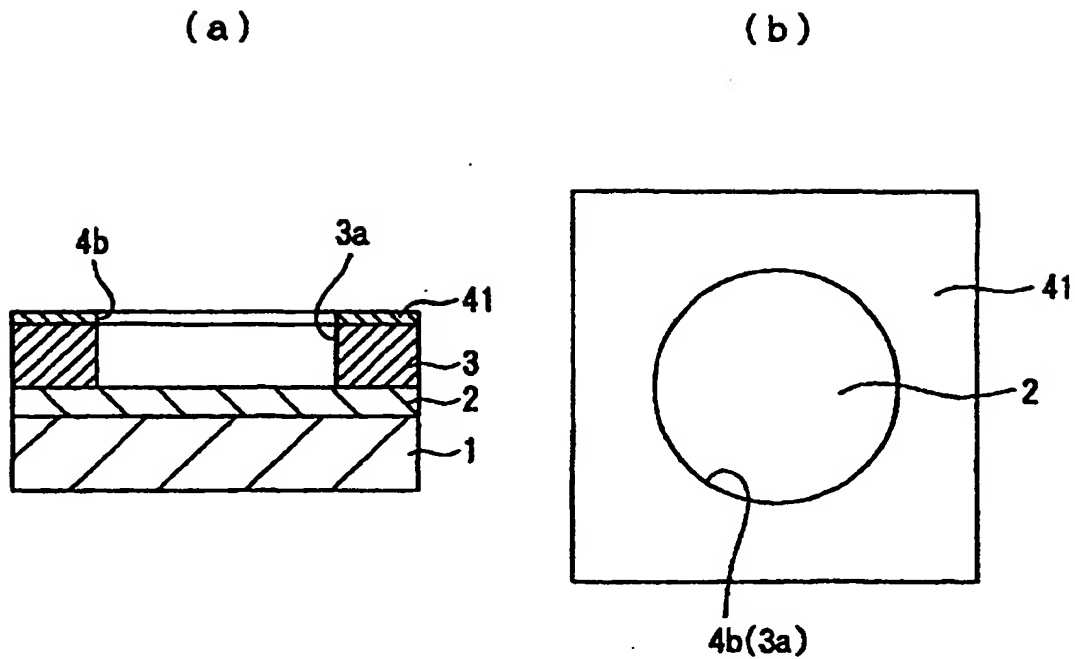
[FIG. 7]



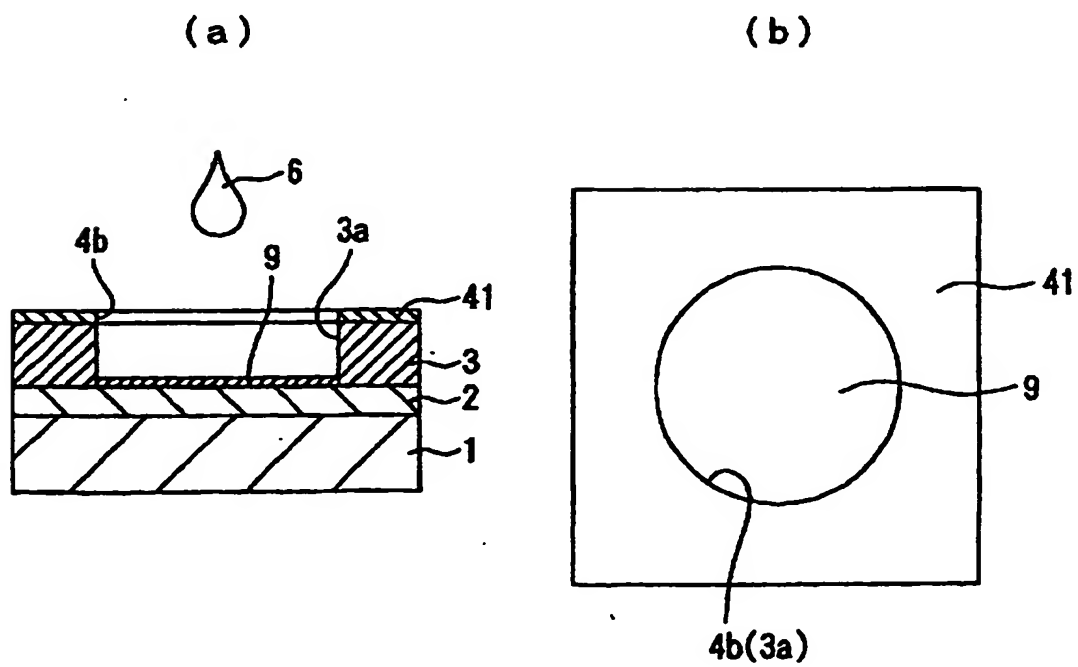
[FIG. 8]



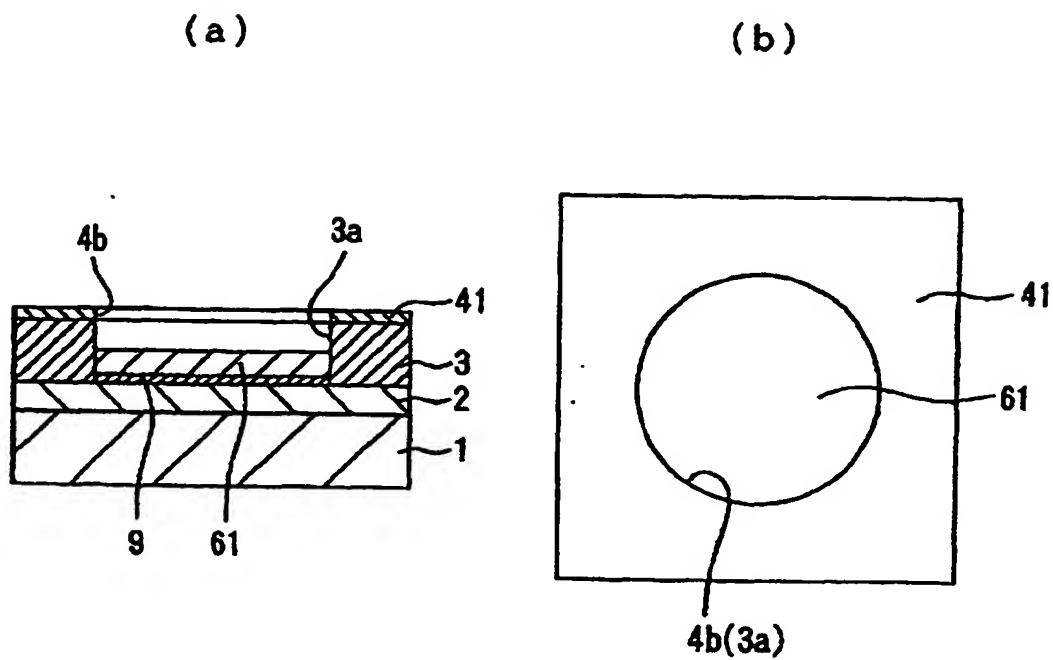
[FIG. 9]



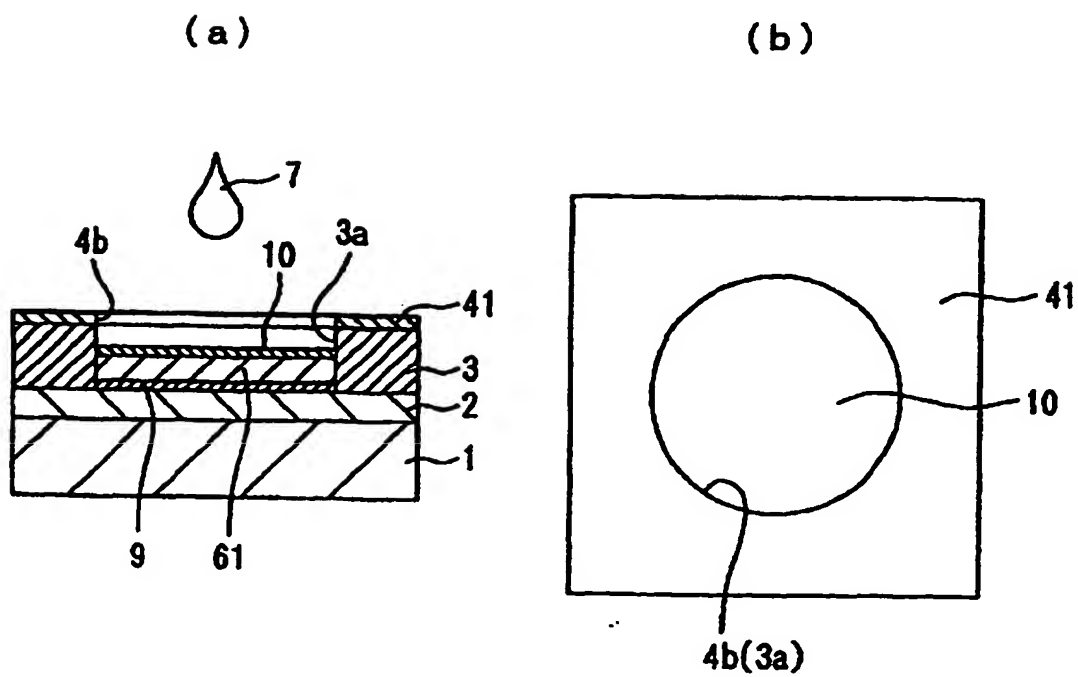
[FIG. 10]



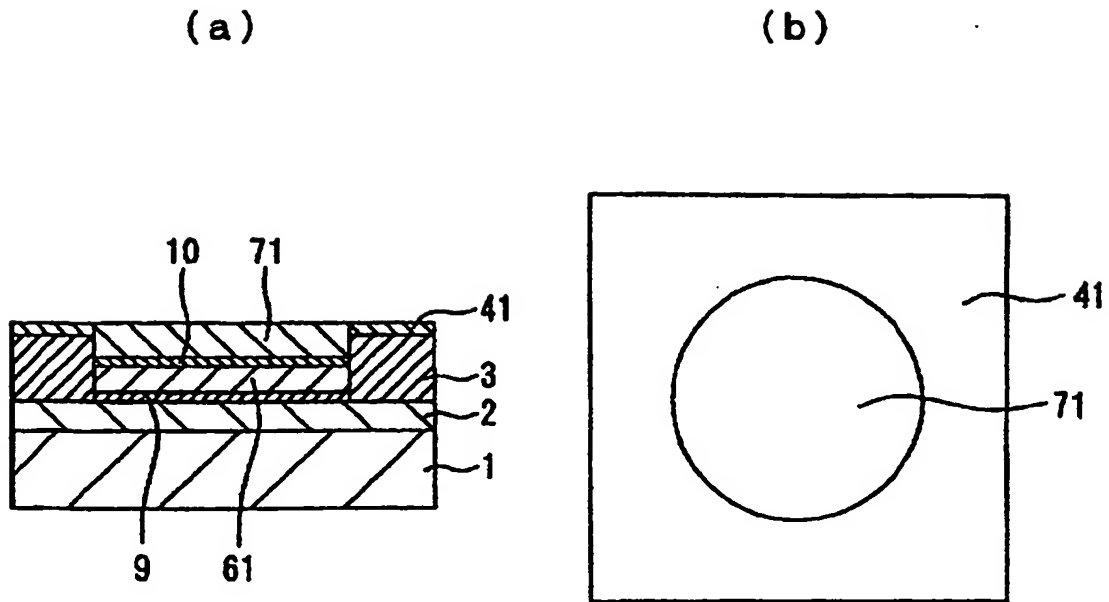
[FIG. 11]



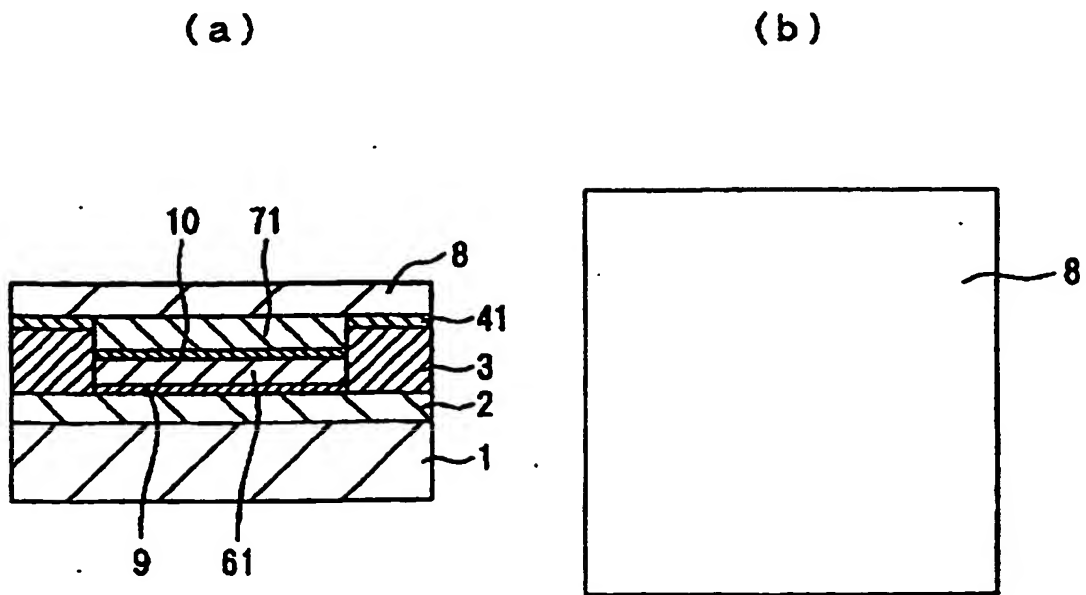
[FIG. 12]



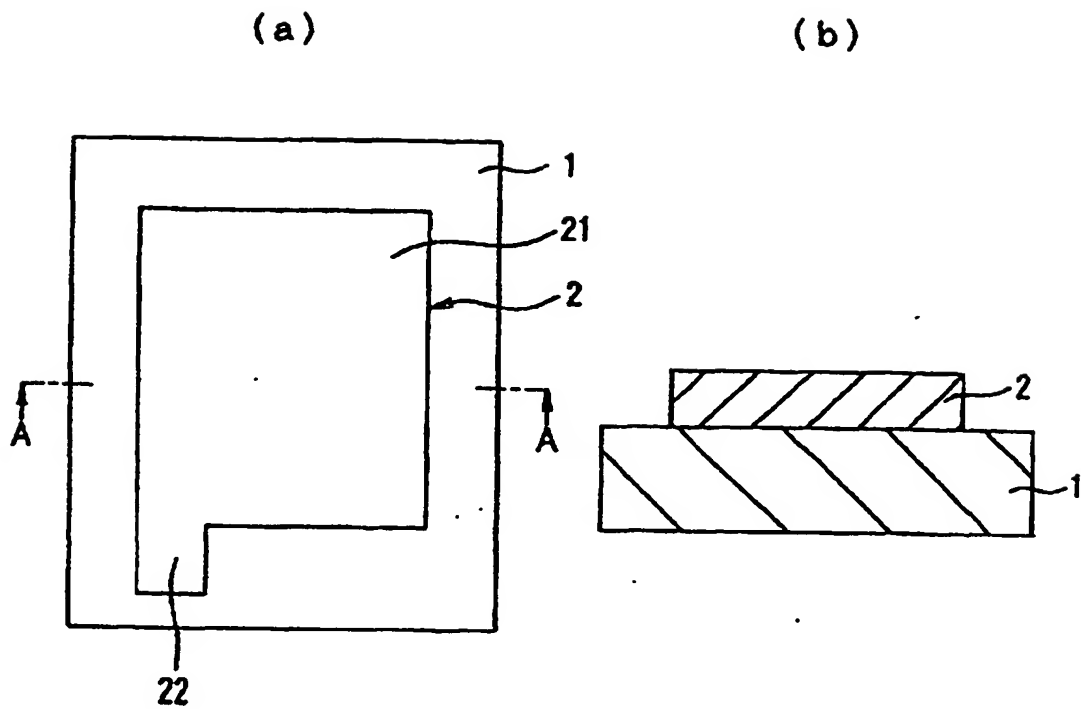
[FIG. 13]



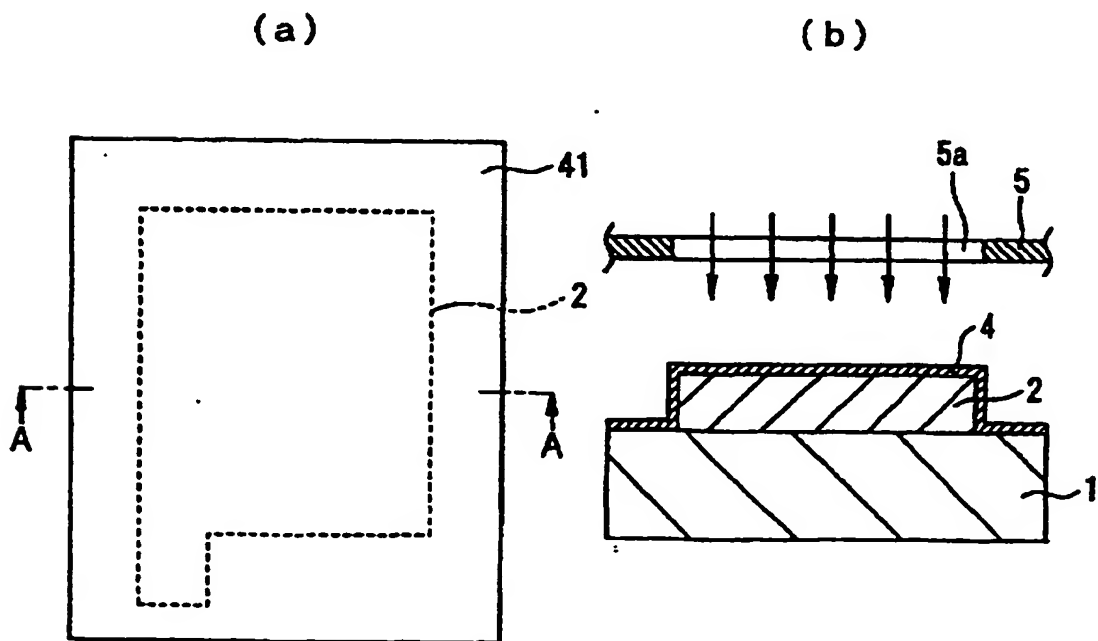
[FIG. 14]



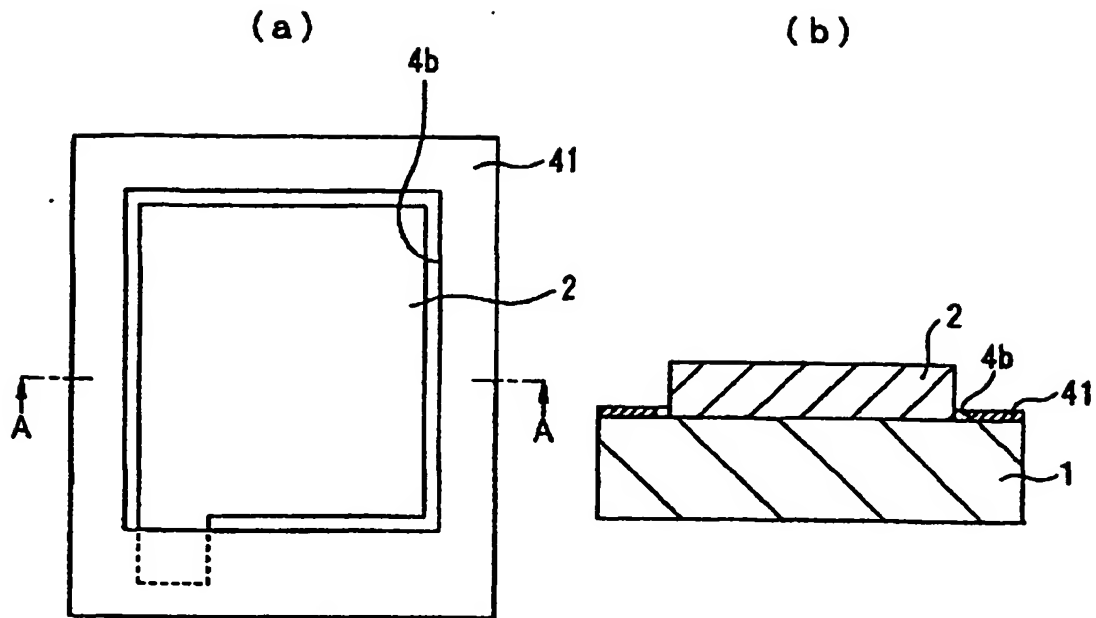
[FIG. 15]



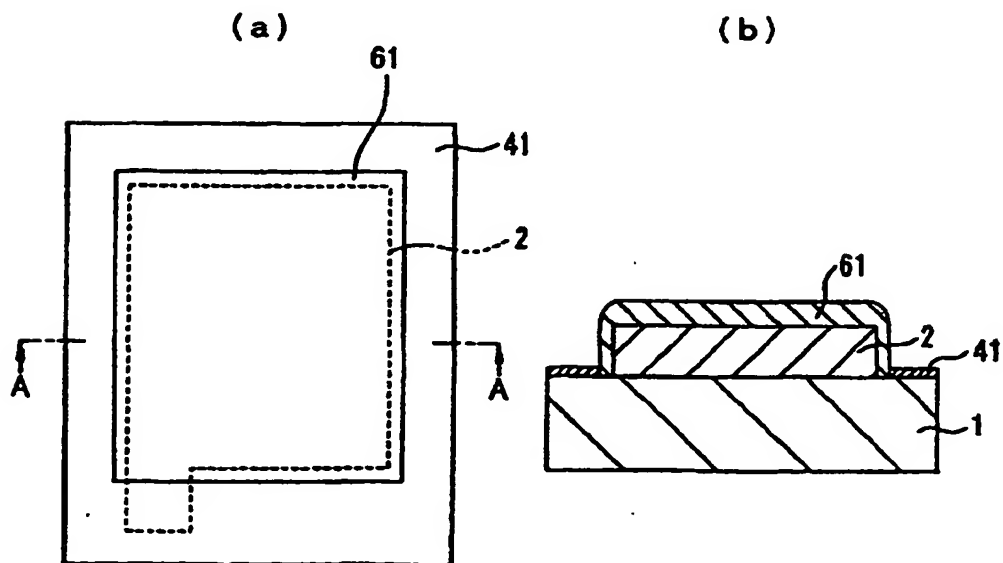
[FIG. 16]



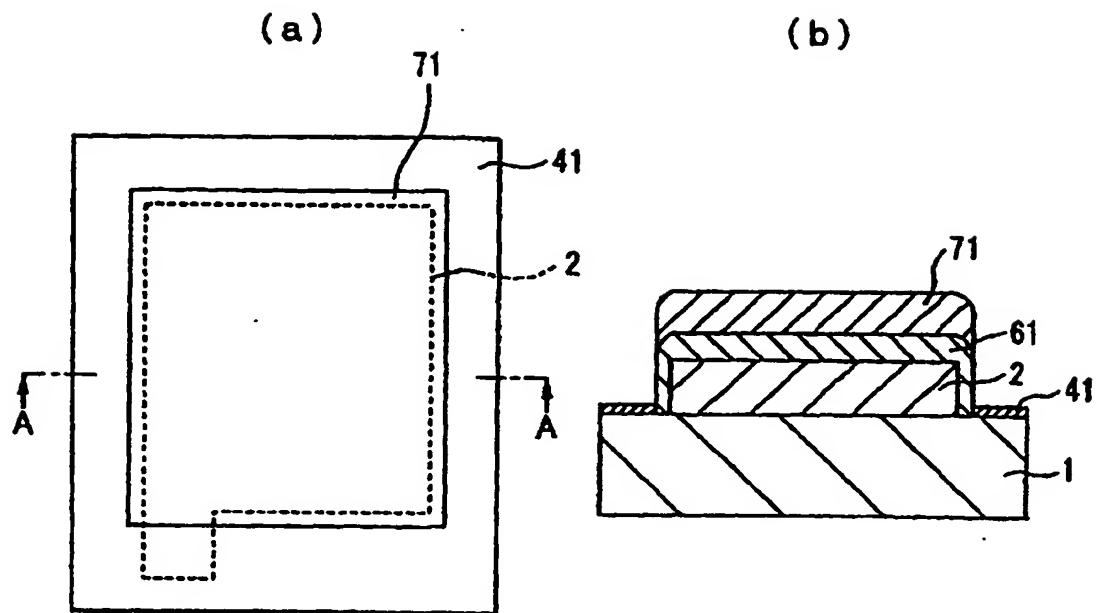
[FIG. 17]



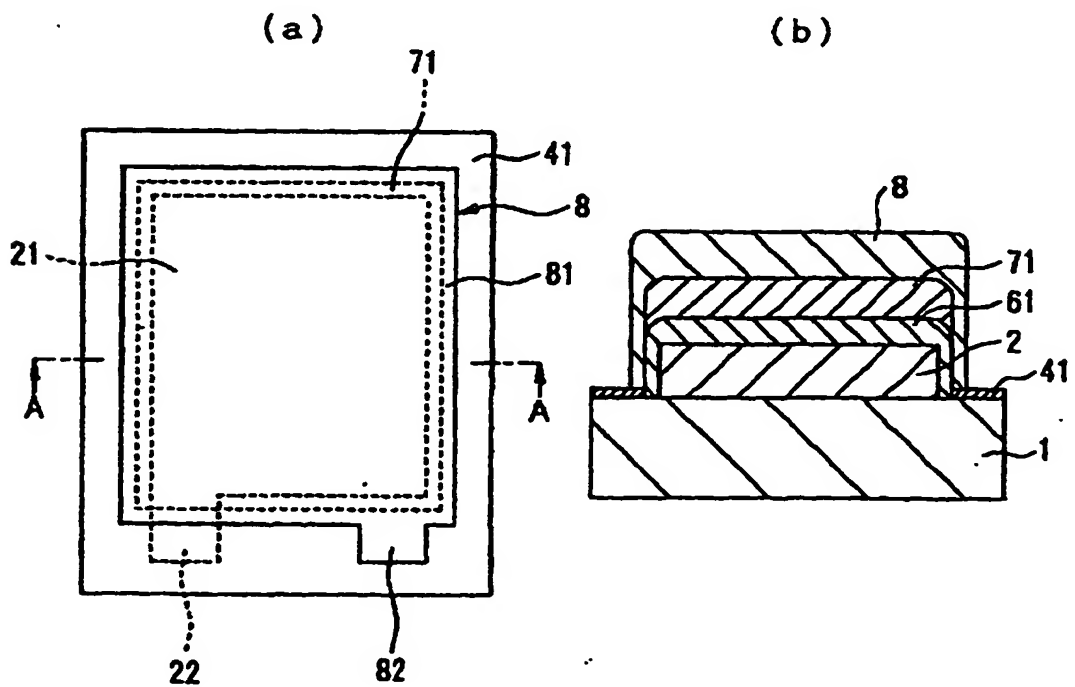
[FIG. 18]



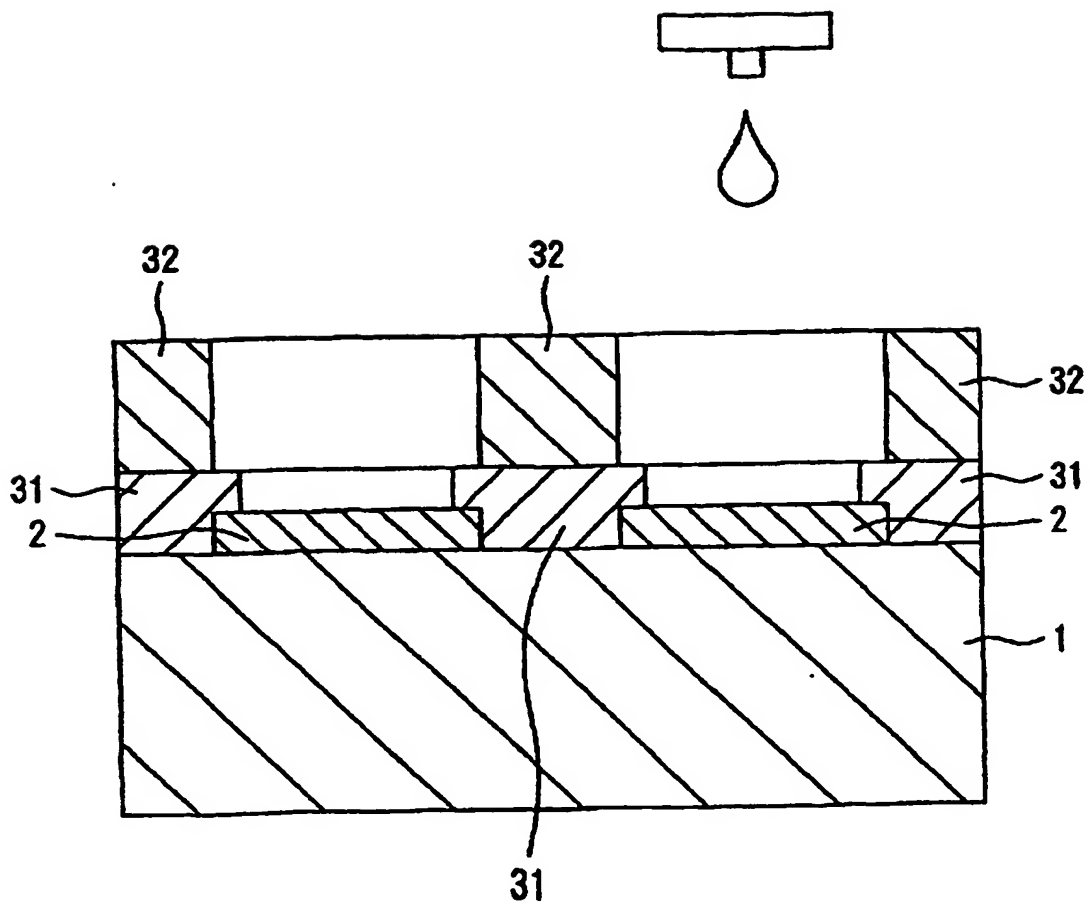
[FIG. 19]



[FIG. 20]



[FIG. 21]



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